PRODUCTION OF CONDUCTIVE POLYMER USING CARBON NANOTUBE

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SUPERVISOR'S DECLARATION

I hereby declare that I have checked this project and in my opinion, this project is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

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ABSTRACT

Polymeric based composite materials have large usage in the industrial scale, which involving improvement of mechanical properties to the alternation of thermal and electrical properties. Carbon nanotubes (CNTs) exhibit excellent mechanical, electrical, and magnetic properties as well as nanometer scale diameter and high aspect ratio, which make them an ideal reinforcing agent for high strength polymer composites. The objectives for this paper are to study the mechanical properties (tensile strength, young modulus and elongation) of conductive polymer, to study the effect of acid and heat treatment process towards the PLA mechanical and electrical properties, to identify effects of different weight percentage of untreated CNTs in PLA matrix and to compare the treated and untreated CNTs mechanical and electrical properties in PLA matrix. The samples prepared are categories into two types firstly using untreated CNTs with Polylactic acid (PLA) with different CNTs compositions and secondly sample prepared from two type of treated CNTs which were using thermal or heat surface treatment and acid surface treatment using hydrochloric acid and the untreated and treated CNTs are mixed into PLA polymer. Method used to produce sample for analysis was by passing through the material in an extrusion molding machine at specific temperature and screw speed followed by injection molding with specific pressure and temperature. The produce sample undergo several analysis and testing which were mechanical testing, Scanning Electron Microscope, Transgravimetric analysis and surface resistivity analysis. From the results it shows that untreated sample with 1.00wt % had higher tensile strength and elongation compared with acid and heat treated CNTs with 1.00wt% CNTs. Meanwhile, Transgravimetric analysis shows that the untreated 1.00wt% CNTs sample had the highest thermal degradation temperature compared to others sample. Surface resistivity analysis for comparing 1.00wt % treated and untreated sample it showed that acid treated sample has the lowest surface resistance with the value of 2.06826 Ohm/sq. The results obtained from the experiments is reliable and shows a pattern of data that can be used for further improving the research in obtaining the optimum amount of CNTs for better future research study. The data also shows that acid treatment with nitric acid is not proper for PLA polymer due to it degradation property when acid and basic impurities are present. In future improvement of research paper alternative treatment could be found in improving CNTs surface properties.

ABSTRAK

Bahan-bahan komposit berasaskan polimer mempunyai penggunaan yang besar dalam skala industri, yang melibatkan peningkatan sifat-sifat mekanik silih sifat haba dan elektrik. Nanotube karbon (CNTs) mempamerkan cemerlang sifat-sifat mekanikal, elektrik, dan magnet serta garis pusat skala nanometer dan nisbah aspek yang tinggi, yang menjadikan mereka ejen yang ideal memperkukuh bagi komposit polimer kekuatan tinggi. Objektif kertas ini adalah untuk mengkaji sifat-sifat mekanik (kekuatan tensil, modulus muda dan pemanjangan) polimer konduktif, untuk mengkaji kesan asid dan proses rawatan haba terhadap sifat-sifat mekanik dan elektrik PLA, untuk mengenal pasti kesan peratusan berat badan yang berbezaCNTs tidak dirawat di PLA matriks dan bandingkan CNTs dirawat dan tidak dirawat mekanikal dan sifat-sifat elektrik di PLA matriks. Sampel yang disediakan adalah kategori kepada dua jenis yang pertama menggunakan CNTs tidak dirawat dengan asid Polylactic (PLA) dengan komposisi CNTs berbeza dan kedua sampel yang disediakan daripada dua jenis CNTs dirawat yang menggunakan permukaan rawatan haba atau haba dan rawatan permukaan asid menggunakan asid hidroklorik dan tidak dirawat dan dirawat CNTs dicampurkan ke dalam PLA polimer. Kaedah yang digunakan untuk menghasilkan sampel untuk analisis adalah melalui bahan dalam mesin pengacuan penyemperitan pada suhu tertentu dan kelajuan skru yang diikuti oleh pengacuan suntikan dengan tekanan dan suhu tertentu. Sampel hasil menjalani beberapa analisis dan ujian yang ujian mekanikal, Pengimbasan Mikroskop Elektron, Transgravimetric analisis dan analisis kerintangan permukaan. Daripada keputusan, ia menunjukkan bahawa sampel yang tidak dirawat dengan% 1.00wt mempunyai kekuatan tegangan yang lebih tinggi dan pemanjangan berbanding dengan asid dan dirawat haba CNTs dengan CNTs% 1.00wt. Sementara itu, Transgravimetric analisis menunjukkan bahawa CNTs sampel% tidak dirawat 1.00wt mempunyai suhu degradasi haba tertinggi berbanding dengan sampel yang lain. Analisis permukaan kerintangan untuk membandingkan% 1.00wt dirawat dan sampel yang tidak dirawat, ia menunjukkan bahawa sampel asid yang dirawat mempunyai permukaan rintangan yang terendah dengan nilai 2,06826 Ohm / persegi. Keputusan yang diperolehi daripada uji kaji boleh dipercayai dan menunjukkan corak data yang boleh digunakan untuk meningkatkan lagi penyelidikan dalam mendapatkan jumlah optimum CNTs untuk kajian masa depan yang lebih baik. Data juga menunjukkan bahawa rawatan asid dengan asid nitrik tidak wajar untuk PLA polimer kerana harta degradasi IT apabila asid dan kekotoran asas hadir. Dalam peningkatan masa depan rawatan alternatif kertas penyelidikan boleh didapati dalam memperbaiki sifat-sifat permukaan CNTs.

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A	Fitted constant
c	The conductivity of the composites,
V	Carbon nanotube volume fraction,
Vc	Carbon nanotube volume fraction at the percolation threshold
˚C	Temperature measurement
ρ_s	Surface Resistivity
U	Voltage
L	Length
I_S	Surface Current
D	Diameter
M	Concentration
V	Volume

LIST OF ABBREVIATIONS

CNTs	Carbon Nanotube
PLA	Polylactic acid
SEM	Scanning Electron Microscope
UTM	Universal Testing Machine
TGA	Transgravimetric Analyzer

CHAPTER 1

INTRODUCTION

1.1.1 INTRODUCTION

Conducting polymer research dates back to the 1960s, when Pohl, Katon, and their coworkers, first synthesized and characterized semiconducting polymers. The discovery of the high conductivity of polysulfurnitride (SN)x, a polymeric material containing interesting electrical properties, was a step forward for research in conducting polymers. Historically, people have referred to polymer as plastic. Technically, plastic refers to the state in which a material is deformed plastically and does not return to its original underformed state (James C. Gerdeen et al., 2006). Polymeric based composite material has a large usage in the industrial scale, which involving improvement of mechanical properties to the alternation of thermal and electrical properties. It is also necessary to find and alternatives to produce conductive polymer using carbon nanotube due to market demand and recent abundant research done on carbon nanotube as nano-filler.

Conductive composite is well fitted to carbon nanotube (CNTs) this is due to several factors such as exhibit high aspect ratio and high conductivity. Carbon nanotubes (CNTs) exhibit excellent mechanical, electrical, and magnetic properties as well as nanometer scale diameter and high aspect ratio, which make them an ideal reinforcing agent for high strength polymer composites. (Nanda Gopal Sahooa et al, 2010)

Percolation theory predicts that there is a critical concentration at which composites containing conducting fillers in insulating polymers become electrically conductive.

According to percolation theory Eq (1.1):-

$$c = A(V-Vc) \tag{1.1}$$

c = the conductivity of the composites,
V = CNT volume fraction,
Vc = CNT volume fraction at the percolation threshold
(Percolation threshold has been reported to ranging from 0.0025 wt% to several wt % -Sandler JKW et al)

A= fitted constant.

The percolation threshold for the electrical conductivity in polymer-CNT nanocomposites depends on dispersion, alignment, aspect ratio, degree of surface modification of CNTs, polymer types and composite processing methods.

This research has chosen polylactic acid (PLA) compared with other biodegradable polymer such as poly(ε-caprolactone) (PCL) due the several factor. PLA compared to other biodegradable polymer are higher biodegradability and better mechanical properties such as tensile strength, results in a material whose properties make it easier to process and diversifies its possible applications such as chemotherapeutic (E. Laredo et al, 2010).

1.2 PROBLEM STATEMENT

Recent, industrial grow had demanded the research on conductive polymer with higher conductivity and improve properties of polymer polymeric films are inherently insulating, they can become charged during ground-based manufacturing and handling as well as in space due to the orbital environment. The material can then behave like a capacitor and discharge in a single event causing considerable damage to surrounding materials and electronics on the vehicle.

The current state-of-the-art to impart electrical conductivity while maintaining a low and high optical transparency has been through the use of conductive coatings such as indium–tin oxide (ITO). While exhibiting high surface conductivity, these coatings are rather brittle and make handling difficult. Once the coating is broken (cracked) by handling or on orbit, the conductive pathway is lost. Conductive Polymer is the best solution for this problem due high transparency.

1.2 RESEARCH OBJECTIVE

In general, this research is related towards finding properties of mechanical properties conductive polymer (PLA/Carbon Nanotube) and it can be distinguished into four particular scopes:

i. To study the mechanical properties (tensile strength, modulus of elasticity and yield) of conductive polymer.
ii. To study the effect of acid and heat treatment process towards the PLA mechanical and electrical properties.
iii. To identify effects of different weight percentage of untreated CNTs in PLA matrix.
iv. To compare the treated and untreated CNTs mechanical and electrical properties in PLA matrix

1.3 SCOPE OF STUDY

In achieving, the first objective which is to study the mechanical properties of conductive polymer several test will be tested towards the specimen such as simple stress and strain behavior (William D. Callister et. al., 2008). From this test the stress strain behaviors can be plotted in graphical view where the effect of stress and strain can be clearly seen.

Meanwhile, in achieving the second objective the treatment process related in treating the CNTs using acid and heat had been identified. By using this treatment method the sample contain CNTs which are treated are prepared.

Third objective can be achieved by making different weight percentage of CNTs which are 0.5wt%, 1.0wt% and 1.5wt% in PLA matrix. The different composition of CNTs in PLA matrix will be studied by comparing its mechanical properties and electrical properties by using results from independent tested results.

Final objective is achieved, by comparing the same weight percentage of CNTs in the acid, heat and untreated sample to obtain the needed data. The data obtain from this three type of sample will give a better comparison for sample which has undergo CNTs treatment process and untreated CNTs.

1.4 RATIONALE & SIGNIFICANCE

Rationale of this research is that it can improve the capabilities of biodegradable polymer nowadays not only to function as plastic bag and everyday usage material. The properties of PLA which are environmental friendly give an upper hand in selecting a proper polymer matrix in the production of conductive polymer.

This research will identify the effects of CNTs on the polymer matrix. Furthermore, this research will be able to identify the effect of treated CNTs towards PLA matrix which will give an overview on the future improvement of conductive polymer application and usage.

Improving PLA properties also is another significant outcome that can be expected from this research. This is due to the improvement that can be seen from the usage of CNTs in PLA matrix will give and improvement not only on application of PLA nowadays but also in future.

CHAPTER 2

LITERATURE REVIEW

2.1 POLYMER

Polymer can be defined as material which contains many unit of monomer example polyethylene which builds from many unit of ethylene (monomer) (James C. Gerdeen et al., 2006). The most known properties are function as an insulator and has high melting and boiling point. (Mohd Hamzah Harun et al, 2007). From description, of this polymer that conductive polymer is a venture of chemical engineering as said in Mohd Hamzah et al.(2007) article about scientists discovery on electrical properties of conjugated polymer that called 'polyacetylene' which become highly electrically conductive after undergoing a structural modification process called doping structural modification process called doping.

Several properties of poly(lactic-acid), has made it one of the most attractive and useful biodegradable polymer, such as biodegradable, biocompatible and compostable polyester derived from renewable resources such as corn, potato, cane molasses and beet sugar. It is one of the most promising environmentally friendly thermoplastics. (K. Chrissafis, 2010).

Polylactide, obtained from the polymerization of lactic acid (2-hydroxypropionic acid, $CH3–CH(OH)–COOH$), is also known as polylactic acid, PLA. It has recently entered worldwide in the market for use as a biodegradable plastic .Due to the comparable mechanical properties with standard thermoplastics such as polyethylene terephthalate (PET) and polyvinyl chloride (PVC), PLA could represent a good candidate for the replacement of petrochemical thermoplastics. (Saveria Santangelo et al., 2010).

PLA also a thermoplastic polymer, aliphatic polymer and can be derived from renewable sources such as starch and is a sustainable alternative to petrochemical-derived products. PLA has been found to have good stiffness and strength and is being used in several applications, such as food packaging, water and milk bottles, degradable plastic bags as well as in automotive applications. The products made from PLA are bio-degradable and are found to fully disappear in less than 30 days in ideal conditions (Mehdi Jonoobi et al.,2010).

2.2 CARBON NANOTUBE

2.2.1 Introduction Carbon Nanotube

Carbon Nanotube used as nano-fillers in existing polymeric materials to both dramatically improve mechanical properties and create highly anisotropic nanocomposites. They can also be used to create electrically conductive polymers and tissue engineering constructs with the capacity to provide controlled electrical stimulation.

Carbon nanotubes (CNT) are unique, one-dimensional macromolecules, whose outstanding properties have sparked an abundance of research since their discovery in 1991 (S.K. Smart et al., 2005). Single-walled carbon nanotubes (SWCNT) are constructed of a single sheet of graphite (diameter 0.4– 2 nm), while multi-walled carbon nanotubes (MWCNT) consist of multiple concentric graphite cylinders of increasing diameter (2–100 nm) (S.K. Smart et al., 2005). Both SWCNT and MWCNT have high tensile strength, ultra weight and have excellent thermal and chemical stability. Besides that, they also possess semi-conductor electronic properties and metallic properties (S.K. Smart et al., 2005).

2.2.2 Biocompatibility of carbon nanotubes

In these studies, it shows that CNT biocompatibility is shown from the the unique electronic properties of CNT for used in neural applications focusing particularly on neurite extension (S.K. Smart et al., 2005). Neurite extension biocompatibility shows that positively charged ethylenediamine-MWCNT producing the most neurite extension due to the loosely ionic charge (S.K. Smart et al., 2005).

Biocompatibility also shown, in utility of CNT-containing materials as bone biomaterials, by examining the adhesion and function of bone-forming osteoblast cells osteoblast proliferation on nanocomposites of CNT under alternating current stimulation was also investigated. S.K Smart et al.(2005) had identified a research that fabricated conductive polylactic acid (PLA)/MWCNT nanocomposites at 10, 15 and 20% (synthesized via electric arc-discharge) whereby the osteoblast cells were seeded onto the surface and then exposed to alternating current stimulation. Control samples (PLA/MWCNT nanocomposite films) were run without electrical stimulation. Their results showed an increase in osteoblast proliferation and extra-cellular calcium deposition on the nanocomposite.

2.3 METHOD FOR POLYMER PRODUCTION

2.3.1 In situ polymerization processing

Over the last 5 years in situ polymerization in the presence of carbon nanotubes has been intensively explored for the preparation of polymer grafted nanotubes and processing of corresponding polymer composite materials. The main advantage of this method is that it enables grafting of polymer macromolecules onto the walls of carbon nanotubes. In addition, it is a very convenient processing technique, which allows the preparation of composites with high nanotube loading and very good miscibility with almost any polymer type. This technique is particularly important for the preparation of insoluble and thermally unstable polymers, which cannot be processed by solution or melt processing. (Jonathan et al., 2006). In situ polymerization also has the capabilities in improving the mechanical properties of polymer.

Kumar et al.,2010 have synthesized new ultra-strong poly (pphenylene benzobisoxazole) (PBO) composites in the presence of single-wall carbon nanotubes (SWNTs) in poly(phosphoric acid) (PPA) by in situ PBO polymerization. In general, in situ polymerization can be applied for the preparation of almost any polymer composites containing carbon nanotubes which can be non-covalently or covalently bound to polymer matrix. Non-covalent binding between polymer and nanotube involves physical adsorption and wrapping of polymer molecules through van der Waals and p–p interactions.

2.3.2 Covalent Functionalisation and Polymer Grafting Of Nanotubes

Single-Walled carbon nanotube (SWCNs) covalent functionalisation and surface chemistry is an essential factor for nanotube processing and application. (Jonathan et al). Carbon nanotube and the polymer matrix usually has small amount bonding attraction this is due to the relative smooth graphene surface of nanotube. Nanotube, in particular SWNTs, is typically held together as bundle which resulting in poor dispersion in polymer matrices. (Jonathan et al,.2006). Covalent functionalisation is expected to resolve this problem by either modification of surface-bound carboxylic acid groups on the carbon nanotube or direct addition of reagent towards the wall of carbon nanotubes. (Jonathan et al., 2006).

Furthermore, this method has two strategies which are “grafting from” and “grafting to”. The ‘‘grafting from’’ method is based on the initial immobilization of initiators onto the nanotube surface followed by the in situ polymerization of appropriate monomers with the formation of the polymer molecules bound to the nanotube. The advantage of this technique is that polymer–nanotube composites with quite high grafting density can be prepared. However, this method requires a strict control of amounts of initiator and substrate as well as a control of conditions for polymerization reaction. (Jonathan et al., 2006).

The ‘‘grafting to’’ approach is based on attachment of already desired end-functionalised polymer molecules to functional groups on the nanotube surface via different chemical reactions. An advantage of this method is that preformed commercial polymers of controlled mass and distribution can be used. The main limitation of the ‘‘grafting to’’ technique is that initial binding of polymer chains sterically prevents diffusion of additional macromolecules to the surface leading to low grafting density. Also only polymers containing reactive functional groups can be used. (Jonathan et al., 2006).

“Grafting from” strategies has been used in modification of SWNTs with polyethylene (PE) by in situ Ziegler–Natta polymerization. (Tong et al.,2004). In this, modification the SWNTs was functionalized with the catalyst (MgCl2/TiCl4), and then the ethylene was polymerized thereby giving PE grafted SWNTs, which were mixed with commercial PE by melt blending. (Tong et al., 2004). Meanwhile, “grafting to” strategies was used in polymer containing reactive functional groups. For example, Bhattacharyya et al. have developed new fully integrated nanotube–PVA composite materials through the functionalisation of MWNTs by covalently attaching ferritin protein molecules onto the surface of nanotubes.

2.4 APPLICATIONS

2.4.1 Designing sensitive electrochemical sensors

This is whereby conductive polymer, such as Polyaniline(PANI) used to design sensitive electrochemical sensors. It was observed that with an increase of the nanotube concentration, the conductivity of PANI/nanotube films and the current level in the metal-semiconductor devices increase, even at an elevating temperature condition. (Kin-tak Lau et al., 2006)

2.4.2 Power application

Power application, uses conductive polymer to ensure safety and efficient in their system such as proton exchange membrane (PEM) fuel cell, polymeric solar cells, polymeric solar cells LiC batteries, and thermionic emitters. (Kin-tak Lau et al., 2006)

2.4.3 Biomedical material and devices

Conducting polymer can change their property by incorporation of ions and solvent which is a most dependent device to measure conductivity, it is possible to develop and market ion-specific sensors based upon conducting polymers (Mohd Hamzah Harun et al., 2005). Biomedical is a field whereby carbon nanotube hugely used in major area such in the production of biomedical material and devices such as biosensors, drug and vaccine delivery devices. (S.K. Smart et al., 2005)**.**

Conducting polymers also the capabilities in changing electrical energy to mechanical energy example is It is therefore possible for conducting polymers to convert electrical energy into mechanical work oxidation-induced strain of polyaniline and polypyrrole-based actuators has been reported, and the first 'self-contained' actuators (Mohd Hamzah Harun et al., 2005).

2.4.4 Radio Direction and Ranging (RADAR) Application

RADAR uses electromagnetic waves that bounce off a particular target and are collected by a receiver, which analyzes the signal and determines the range, direction, and speed of the object in question (Mohd Hamzah Harun et al.,2007). Reflections occur whenever there is a sharp impedance difference between the medium (usually air) and the object. Metals tend to re-radiate (reflect) the incoming signal. Conducting-polymer camouflage works a little differently, in that it reflects back in a way that it has more continuously variable impedance. A conducting polymer textile used for camouflage has no sharp edges or wings and tends to appear indistinguishable from the surrounding hills and trees and absorbs more than 50% of incident microwave radiation. (Mohd Hamzah Harun et al., 2007). Conducting polymers as radar absorbers in antennas, camouflage, and other types of shielding are of interest to the military.

2.5 LATEST FOUNDING ON CONDUCTIVE POLYMER

Latest founding about conductive polymer are told in E. Laredo et al.(2010) which had spoken about a polymer blend which conduct Direct Current (DC) and Alternating current (AC) electrical conductivity of bionanocomposites based on the immiscible polymer blend poly-(ε-caprolactone)/polylactide (PCL/PLA, w/w 70/30), loaded with multiwall carbon nanotubes (CNT) . From this research, selective location of the CNT in the PCL phase is responsible for the significant improvement of the mechanical properties of this biodegradable blend and its electrical properties are also quite promising for future applications (E. Laredo et al., 2010).

Another founding which is related to conductive polymer is from Saveria Santangelo et al.(2011), in this article they have written on exploring the preparation of novel biodegradable PLA nanocomposites by the use of carbon nanotubes (CNT) and clay as filler, and of evaluating how their mass and electrical transport properties change with respect to the unfilled polymer. From this, article they had concluded that results obtained suggest that clay and CNT exert a synergistic action in improving the polymer properties such as electrical conductivity (Saveria Santangelo et al., 2011.).

2.6 COMPARING PHYSICAL PROPERTIES OF METALS, INSULATORS AND CONDUCTING POLYMERS.

All materials can be divided into three main groups: conductors or metals, insulators and semiconductors. They are differentiated by their ability to conduct or the ability to allow the flow of current. Generally, conducting polymers are classified as semiconductors although some highly conducting polymers, such as polyacetylene, fall into metal range. Table 1 compares some of the physical properties of insulators, semiconductors and conductors. (Mohd Hamzah Harun et al., 2007)

Table 2.1: Comparison of physical properties of metals, insulators and conducting polymers.

Property	**Conducting polymers**	**Metals**	**Insulators**
Electrical Conductivity (S/cm)	$10^{-11} - 10^{3}$	$10^{-4} - 10^{6}$	$10^{-20} - 10^{12}$

al.(2005) that weak interaction and dispersion of acid treated CNTs in PLA matrix. Defeng Wu et al.(2008) also stated in the paper that the surface functionalization of MWCNTs also play an important role in the dispersion and thermal stability of PLA matrix. CNTs also could act as inert filler with respect to thermal decomposition of the PLA matrix which has been explained by Defeng Wu et al.(2008), explanation given is that the reduction in cross linking off the matrix chain or on the other hand CNTs act as added component or impurities such as compatibilizer or remaining catalyst from nanotube synthesis may also be considered.

4.4.6 PLA/CNTs Composite (1.00wt % Heat Treated Carbon Nanotube)

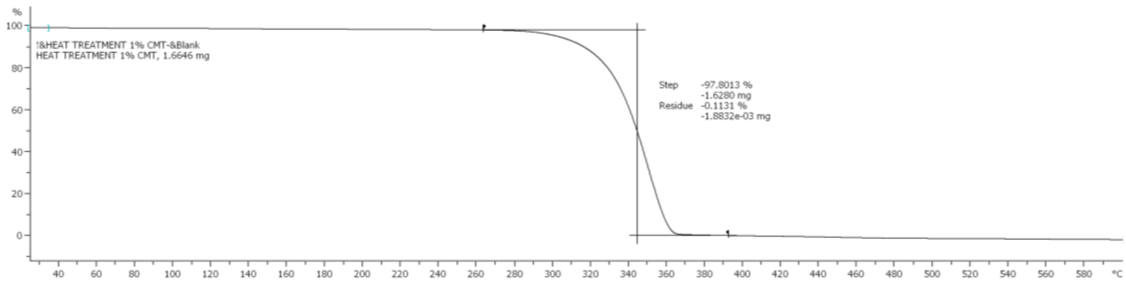

Figure 4.23: Graph of TGA analysis for Percentage of Weight Loss at Different Temperature for Heat Treated CNT (1.0 wt %) /PLA composite

The graph shows the pattern of mass loss in PLA/CNTs composite with 1.00 wt% of heat treated CNTs versus temperature. The graph also shows that the thermal degradation temperature for the composite is higher than 350 C or higher than the pure PLA thermal decomposition temperature. This observation give an indication that heat treated CNTs has better interaction and dispersion in PLA matrix compared to acid treated CNTs.